California Environmental Protection Agency

Air Resources Board

SOP MLD 065

STANDARD OPERATING PROCEDURE FOR ORGANIC AND ELEMENTAL CARBON ANALYSIS OF EXPOSED QUARTZ MICROFIBER FILTERS

Northern Laboratory Branch
Monitoring and Laboratory Division

First Approved Date of SOP: July 29, 2002
Approval Date of Last SOP Amendment:
Revision Number: 0.0

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1.0 SCOPE

This document describes the analysis of exposed quartz microfiber filters for organic carbon (OC) and elemental carbon (EC) using a Desert Research Institute (DRI) Thermal/Optical Carbon Analyzer.

2.0 SUMMARY OF METHOD

The method is based on the preferential oxidation of organic carbon and elemental carbon compounds at different temperatures. Organic compounds are volatilized from the sample deposit in a helium (He) atmosphere at low temperatures, while elemental carbon is not oxidized and removed. The carbon compounds are liberated under temperature and oxidation environments from a small sample using a 5/16 inch diameter punch (0.512 cm^2) taken from a quartz fiber filter. These compounds are converted to carbon dioxide (CO_2) by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO_2). The CO_2 is reduced to methane (CH_4) by passing the flow through a methanator (hydrogen – enriched nickel catalyst). A flame ionization detector (FID) is used to quantify the methane. The optical component of the analyzer is used to correct for pyrolysis of organic carbon compounds to elemental carbon in order to avoid underestimation of OC and overestimation of EC. The sample reflectance and transmission are continuously monitored by a helium-neon laser and a photodetector throughout an analysis cycle. When pyrolysis takes place, there is an increase in light absorption resulting in a decrease in reflectance and transmission. Thus, by monitoring the reflectance/transmission, the portion of the elemental carbon peak corresponding to pyrolyzed organic carbon can be correctly assigned to the organic fraction.

3.0 INTERFERENCES

3.1 The presence of certain minerals can affect the laser correction for pyrolysis. These minerals change color as the sample punch is heated, generally resulting in a sample that is darker. Some minerals may affect the laser reflectance by temporarily changing color or changing the surface texture of the deposit residue. These changes are reversible and highly temperature dependent. Colored organic compounds can affect the laser correction causing increased reflectance as these compounds are removed. The presence of certain elements (Na, K, Pb, Mn, V, Cu, Ni, Co, and Cr) as part of the deposit material has been shown to catalyze the removal of elemental carbon at lower temperatures.

3.2 Water vapor can shift the FID baseline. Allowing adequate time for the sample punch to dry in the analyzer by passing gases over it will eliminate this effect.

3.3 All surfaces are cleaned so that no contamination occurs. Filters are carefully handled in order not to contaminate them.

4.0 APPARATUS AND MATERIALS

4.1 DRI (Desert Research Institute) Thermal/Optical Carbon Analyzer Model 2001

4.2 5/16 inch diameter steel punching tool

4.2 Furnace-4800 Barnstead/Thermolyne Corporation

4.3 Gases:
- (a) Compressed air for valves
- (b) Ultra zero air for FID
- (c) Hydrogen using a hydrogen generator (Whatman 75-34 Hydrogen Generator)
- (e) 10% oxygen balance helium – certified (Airgas, catalog # X02HE902003183)
- (f) Grade 5 helium
- (g) 5% methane balance helium – NIST standard (Scott-Marrin, Inc., catalog # 02-150A-350B)
- (h) 5% carbon dioxide balance helium – NIST standard (Scott-Marrin, Inc., catalog # 02-150A-580B)

4.4 Chemicals:
- (a) Potassium hydrogen phthalate (KHP) (Fisher, catalog # P243-100)
- (b) Potassium hydrogen phthalate (Mallinckrodt, catalog # 6704-02) used as second source
- (c) Sucrose (EM Science, catalog # SX1075-1)
- (d) Manganese dioxide (MnO_2), crystalline, as an oxidizer in the oxygen oven (Nurnberg Scientific, catalog # C5162 or equivalent)
- (e) Nickelous nitrate [$Ni(NO_3)_2 \cdot 6H_2O$], crystalline, used as a reducer in the methanator (Fisher Scientific, catalog # N62-500)
- (f) Chromosorb 60/80 mesh, used as a support for nickel catalyst in

methanator (Supelco, catalog # 2-0165). Both nickelous nitrate and this support are for preparing the reduction catalyst in the methanator

(g) Hydrochloric acid (HCl) concentrated for preparing KHP reagent.

(h) Nanopure water

4.5 Traps:

(a) Oxygen trap (Trigon Technologies, catalog # TTO-100-4) for the helium gas

(b) Hydrocarbon trap (Trigon Technologies, catalog # TTH-200-4) for helium gas

(c) Moisture trap (Trigon Technologies, catalog # TTM-200-4) or other suitable trap for the hydrogen generator

4.6 Porcelain Coors dishes for firing the quartz filters

4.7 Tweezers, flat tip (Millipore, catalog # XX6200006)

4.8 Glass petri dish

4.9 Kimwipes

4.10 Syringes:

(a) Gas–tight 1000 μl and 2500 μl syringes for gas calibration injections (Hamilton, catalog # 81320 and 81420, respectively)

(b) 10 μl and 25 μl syringe for liquid calibration injections (Hamilton, catalog # 80400 and 80030, respectively)

4.11 Aim n Flame lighter by Scripto to light the FID

4.12 Printer paper (8 1/2” x 11”)

4.13 Ink cartridge #20 for a Hewlett-Packard Deskjet 648C printer

5.0 PREPARATION OF STANDARDS

5.1 The following standards are used to calibrate the carbon analyzer: 5% CH_4 in helium, 5% CO_2 in helium, and Potassium hydrogen phthalate.

5.2 KHP is dried at 110°C for two hours before preparation of a solution.

5.3 After the KHP has cooled to room temperature, weigh and transfer 0.3829 g of KHP into a clean, dry, glass 100 ml volumetric flask.

5.4 Dissolve the KHP in the flask with about 50 ml nanopure water.

5.5 Add 0.2 ml of concentrated HCl and dilute to volume with nanopure water.

5.6 Mix the KHP solution thoroughly. This will make an 1800 ppm carbon solution of KHP.

5.7 Label the flask with chemical name, date of preparation, the initials of the chemist preparing the solution, and the exact concentration.

5.8 Store the KHP solution in a refrigerator until it is needed for calibration.

5.9 A second solution of KHP, the control, is prepared the same as the calibration solution using a different source of KHP.

6.0 KEITHLEY DRIVERLINX SOFTWARE SETUP PANEL

6.1 Click on the icon to open the Keithley DriverLINX software. The meter panel is used in setting and checking signal levels, while Digital Input/Output panel (DIO) is used for checking the operation of valves, and sample boat positioning (See Figures 33 – 35, Pages 22 – 23 in OC/EC Instruction Manual).

6.2 Click DIO to open the DIO panel. Select output of channel 1 in digital I/O configuration panel. Click on channel 1 from the digital output panel (middle panel). Then boxes (0 – 7) under output bits can be selected to activate the designated functions of the analyzer. Once turned on, the box will light up. Clicking on the same box will turn off that line.

6.3 The assignment of the output bits:

Carle Valve Load	0
Back Valves	1
Carle Valve Inject	2
Front Valves	3
Sample Oven Fan	4
Sample Load	5
Sample Calibrate	6
Sample Analyze	7

7.0 SYSTEM LEAK CHECKING

7.1 The two toggle shut-off valves in conjunction with the System Oven Pressure digital panel meter (DPM) located on front of the instrument above the rotameters are used for detecting leaks in the analyzer. The Oven Outlet toggle valve is located on the right side panel. The Oven Inlet toggle is on the front of the instrument.

7.2 Make sure that He-1, He-2, and the pneumatic air are flowing and that the bridge of the sample boat inlet is sealed. If not, manually switch the sample boat to “Calibrate” to ensure the bridge is sealed.

7.3 Close (flip downward on the handle) the Oven Outlet toggle valve. The Sample Oven Pressure should increase. When the pressure reaches about 5 psig, close the Oven Inlet toggle. The pressure should not decline very much over several minutes, if so there may be a leak. Normally, the areas where leaks are prone are the Teflon ferrules around the thermocouple push rod and the quartz oven inlet and outlet. Tightening the nut should stop the leak. Also, check the septum ports. The two remaining areas are the top and bottom seals of the quartz oven cross. If the leak persists, the oven may have a crack.

7.4 When the system leaks checks are satisfactory, open the toggles to re-establish flow.

8.0 FLOW BALANCING

8.1 Three needle valves on the analyzer’s right side panel provide adjustments needed to balance the flow.

8.2 Make sure that the sample boat inlet bridge is closed, and that the flow rates have been set correctly and all the gases are flowing.

8.3 Set the Watlow Controller Settings as follows: warm up the FID temperature to 125◦C, heat up the oxidation and methanator ovens stepwise in approximately 150◦C increments with approximately 20 minute holding time at each step until the oxidation oven is at 900◦C, and the methanator is at 420◦C. The temperature can be set by holding down on the set button of the controller and using the up or down arrows to adjust the setting (See Pages 47 – 52 in OC/EC Instruction Manual).

8.4 Turn on the Front valves (I/O line 3) at the Keithley DIO panel and note the absence of ball movement at the He-2 rotameter. If the ball jumps up, turn the front (He/O2/He adjust) needle valve clockwise slightly. If the ball drops, turn the needle valve counter clockwise. Turn off the Front valves and let the flow stabilize for a couple of minutes. Repeat this step until little or no ball movement is observed (See Figures 33 – 35, Pages 22 – 23 in OC/EC Instruction Manual).

8.5 Turn on the Back valves (I/O line 1) at the Keithley DIO panel. Adjust the middle (oven flow adjust) needle valve until the System Oven pressure is approximately 1 psig. Slightly higher or lower pressures are not critical.

Allow the pressure to stabilize a few minutes.

8.6 Turn off the Back valves and observe the System Oven pressure. There should be little or no change. Adjust the rear (vent adjust) needle valve to 1 psig. Repeat this step as necessary and allow a few minutes between adjustments.

9.0 CALIBRATION

The instrument is calibrated every six months or when the gas standard is changed whichever comes first. The following are used to calibrate the instrument: 5% CO_2 in helium, 5% CH_4 in helium, and KHP. The CH_4 in helium is also used as the end-of-run calibration automatically injected by the instrument. In addition, the manual calibration injections of 5% CO_2 in helium and 5% CH_4 in helium are performed at the beginning and ending of each analysis day to verify proper analyzer performance.

9.1 A 5% CO_2 in helium gas is injected in the following volumes: 100 μl, 200ul, 500 μl, 1000 μl, and 1500 μl, respectively.

9.2 A 5 % CH_4 in helium gas is injected in the following volumes: 100 μl, 200 μl, 500 μl, 1000 μl, 1500 μl, respectively.

9.3 Then an 1800 ppm carbon KHP standard is used and is injected in the following volumes: 5 μl, 10 μl, 15 μl, and 20 μl, respectively. This gives a concentration of carbon as 9, 18, 27, 36 μg, respectively.

9.4 The gas standard concentrations are corrected for temperature and pressure at the laboratory conditions using the Ideal Gas Law and certified percent concentration of gas in cylinder.

9.5 The injection peak counts divided by the calibration peak counts is calculated, and the slope is determined by plotting calculated carbon in μg vs. peak area/calibration area. The line is forced through zero.

9.6 The slope value determined from the three calibration standards is entered into the “carbon.par” table (ASCII file).

9.7 The control standard, 10 μl of 1800 ppm carbon KHP, is injected onto a clean blank filter punch and analyzed to check the calibration. This source is different from the KHP calibration standard. Once the control value is within ± 10 % of its true value, the check standard can be run.

9.8 The check standard, 10 μl of 1800 ppm carbon KHP, is placed on to a filter punch on the quartz boat. The check standard should be within

±10 % of its true value before continuing to analyze samples.

9.9 A 5% CO_2 in helium or 5% CH_4 in helium gas is analyzed before analyzing samples to check the proper analyzer performance. The standards should be within ± 10% of their true value before continuing to analyze samples.

10.0 SYSTEM BLANKS

10.1 System blanks are analyzed once a week to check to see if the system is clean.

10.2 A blank filter punch is placed in the boat. After baking the system several times, the analysis is started. The system blank should be < 0.2 μg total carbon before analyzing any samples.

11.0 ROUTINE OC/EC ANALYSIS

11.1 Check all the gases to make sure there is enough gas for the day. Turn on the gases and adjust the regulators on the gas tanks. Also, check the water level on the hydrogen generator and add water if needed.

11.2 Increase the H_2 flow to the higher setting as marked on the rotameter (approximately 4.4). Wait for several minutes for the flow to stabilize. Light the FID with a butane lighter placed over the FID stack. A light pop sound indicates that the flame is lit. Check that the FID is lit by holding the bottom of a small beaker or a pair of tweezers over the FID exhaust stack and watching for condensation. After about 10 minutes at the high flow, turn the H_2 rotameter to 3.4, the operating setting.

11.3 Check all gas flows at the analyzer. The correct settings are located on each rotameter. Adjust through the center of the ball.

11.4 On the computer, click the **DRICarb** shortcut icon to start the carbon program.

11.5 Leak test the system (See Section 7.0). Make sure the sample boat position is in the calibration position so that the bridge is closed before performing test. Once the leak test is satisfactory, open the toggles to re-establish flow.

11.6 Balance the flow by adjusting the sample oven pressure to approximately 1.0 psig (See Section 8.0).

11.7 Once the flow has been balanced, a clean blank filter punch can be loaded onto the boat, and the oven can be baked several times. This can be done by clicking on the analysis button on the computer screen, selecting sample, then **cmdBakeOvenNIOSH**. Click OK, and then run. Repeat the bake oven procedure at least three times.

11.8 Make sure that the printer has enough paper, the printer cartridge is okay, and the printer is on.

11.9 Once the oven has been baked, a 5% CO_2 in helium or 5% CH_4 in helium gas standard can be analyzed. Instead of selecting sample, calibrate is selected in the analysis program and **cmdCalib-HeO2** or **cmdCalib-HeOnly** from the command table. Once the software indicates to do so, load a 1000 μl syringe with 5% CO_2 in helium or 5% CH_4 in helium, and then inject into the septum port of the analyzer only after the software has prompted to do so.

11.10 After the gas standard has been analyzed, 10 μl of an 1800 ppm carbon KHP control standard is analyzed. Sample is selected on the analysis program and **cmdNIOSH** from the command table. The analysis page containing the fields, sample ID, punch area (1.0 cm^2), deposit area (1.0 cm^2), and Tech initials are filled in. Click OK and then run. When the software has prompted to do so, load the 10 μl of KHP slowly on to the filter punch. Click OK and then enter the delay time required to dry the liquid standard on the filter punch. For each μl of liquid on the filter punch, 60 seconds of drying time (delay time) is required before the analysis will proceed. In this case, enter 600 seconds and click OK.

11.11 Once the KHP standard has been analyzed and is within limits, the samples can be analyzed.

11.12 Make sure that the tweezers, punching tool, and surface area used to punch on are thoroughly wiped clean with a dry kimwipe.

11.13 Remove the sample petri dish from the refrigerator. On the computer screen, record the site name, sample ID (barcode), punch area, filter exposure area, and chemist's initials. Remove the filter from the petri dish with tweezers onto a glass petri dish. A sample punch is removed by gently pushing down the punching tool. Rock the punching tool slightly to make sure that the punch is completely cut. This will leave the sample punch inside the punching tool. Place the punching tool on a clean surface and return the filter to the petri dish. Remove the sample punch from the punching tool by grasping the bottom edge with the tweezers. Place one sample filter punch in the sample boat, and gently push the sample punch using the large end of a pasteur (glass) pipet to make sure that the sample punch is seated in the well of the boat.

11.14 Click OK after loading sample punch. Then click OK when the software prompts for delay time. The default value is 60 seconds. The sample will go through the sample analysis.

11.15 Wipe the tweezers, petri dish, and punching tool with a clean kimwipe, and return the sample petri dish to the refrigerator.

11.16 Log in the sample ID, date sampled, site name, date analyzed, and chemist initials into the lab notebook.

11.17 At the end of the run, a three page report will print out which includes the peak areas, final results, and the thermogram.

11.18 A duplicate sample is run for every ten samples. A second filter punch is taken from the filter and analyzed.

11.19 Once the samples are analyzed for the day, a 1000 μl of 5% CO_2 in helium or 5% CH_4 in helium is analyzed for the end of day check. Use the alternate gas standard from the one used in the morning and the alternate command program used in the morning.

11.20 Once the end of day calibration run has printed, exit the carbon program. Shut off the toggle valves on the instrument for the Air, Cal Gas, and He/O_2. Then close the gas supply valves for the respective gases.

11.21 From the report print out, the results are entered into the Laboratory Information Management System (LIMS).

12.0 PROGRAM SOFTWARE

12.1 The OC/EC analysis program reads command sequences from and writes data to an Access database file. This file is **C:\Carbon\Access\carbon.mdb**. Clicking on the **DriCarb** shortcut icon will open this file to start the analysis.

12.2 The parameter file, **carbon.par**, is an ASCII file which contains analyzer specific information. This is where the calibration slope can be entered. The user can only read this file by using the Note Pad word processor.

12.3 The command tables are in Microsoft Access. Each command table has all the steps for the analysis program. They contain all of the information for opening and closing the Carle valve, Back valve, Front valve, sample oven fan setting, and sample position setting (See pages 36 – 39, OC/EC Instruction Manual). Following are all of the command tables: **cmdBakeOvenImprove**, **cmdBakeOvenNiosh**, **cmdCalib-HeO2**, **cmdCalib-HeOnly**, **cmdImprove**, and **cmdNiosh**.

13.0 PREPARATION OF FILTERS

Filters are pre-fired for the OC/EC analysis before they are placed into the filter holders and shipped out to the field.

13.1 A Thermolyne 4800 Furnace is set to a temperature of 900°C.

13.2 Quartz 47mm filters (Whatman Cat No. 1851047) are visually checked for damage or holes. Several inspected filters are placed into a porcelain dish using tweezers.

13.3 The porcelain dish with the quartz filters is placed into the furnace oven.

13.4 After the oven reaches a temperature of 900°C, the porcelain dish with the quartz filters is baked for four hours.

13.5 Once the filters have baked for four hours at 900°C, the furnace oven is turned off.

13.6 Remove the porcelain dish with filters, after the oven has cooled off, the next morning.

13.7 The filters are removed from the porcelain dish with tweezers, being careful not to damage any of the filters, and place them into a 50mm petri dish and cover dish.

13.8 Place the petri dish containing the filters into a desiccator for storage until use.

14.0 LIMIT OF DETECTION

The Limit of Detection (LOD) for the method is determined initially during method development. The LOD is verified annually, or when there is a modification to the instrument that will affect its performance.

14.1 The LOD for the OC/EC instrument was determined by analyzing seven replicates of a KHP standard solution.

14.2 A 1μl of a 450 ppm carbon KHP standard solution was injected onto a clean baked filter punch on the boat. This was repeated until seven replicates were analyzed.

14.3 The standard deviation was determined for the seven replicates.

14.4 The standard deviation times the student T value (3.143 for seven replicates) equals the LOD (See Section 15.0, equation 15.6).

15.0 FORMULAS AND CALCULATIONS

15.1 Ideal Gas Law:

$$n = \frac{PV}{RT} = \frac{\left(\frac{P_a}{760}\right)\left(10^{-6}\right)}{0.08206\left(T_a + 273.15\right)}$$

where,
n = moles/volume of gas
P_a = ambient pressure in mm Hg
T_a = ambient temperature in $^\circ$C
V = volume of gas
R = gas constant

15.2 To determine the calibration slope, the graph of μg of C (carbon) vs. injection peak counts/calibration peak counts is plotted.

15.3 Carbon values per punch are converted to μg C/cm^2 by:

$$\mu g\ C/cm^2 = \frac{\mu g\ C/punch}{punch\ area\ in\ cm^2}$$

15.4 Carbon values are converted to μg C/filter by:

μg C/filter = (μg C/cm^2)(filter exposure area in cm^2)

15.5 To determine the micrograms of carbon per cubic meter (μg/m^3):

$$\mu g/m^3 = \frac{\mu g\ C/filter}{flow\ rate\ in\ m^3}$$

Or

μg/m^3 = μg of C (carbon)/punch area in cm^2 x (filter exposure area in cm^2)/flow rate in m^3

15.6 Limit of Detection (LOD) = (standard deviation) x (3.143)

16.0 REFERENCES

16.1 Atmoslytic Inc, DRI Model 2001 OC/EC Carbon Analyzer Instruction Manual, October 2001.

16.2 Birck, M.E. and R.A. Cary, "Elemental Carbon-Based Method for Monitoring Occupational Exposures to Particulate Diesel Exhaust", October 3, 1996, Aerosol Science and Technology.

16.3 U.S. Environmental Protection Agency, "PM2.5 Speciation Trends Network Special Study", April 4, 2001.

16.4 "Elemental Carbon (Diesel Particulate) 5040", NIOSH Manual of Analytical Methods (NMAM), Fourth Edition.

16.5 U.S. Environmental Protection Agency, "Definition and Procedure for the Determination of the Method Detection Limit – Revision 1.11", Pt. 136, Appendix B.